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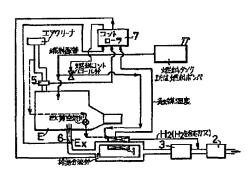
### (54) NITROGEN OXIDE REDUCING DEVICE FOR INTERNAL COMBUSTION ENGINE

#### (57) Abstract:

PURPOSE: To deoxidize and purify the NOx in the exhaust gas directly by the H2 from a hydrogen generator under the exhaust gas low temperature ambiance so as to reduce the NOx, by composing the system to make a part of a hydrocarbon fuel converted into a hydrogen gas to feed by a reformer catalyst converter.

CONSTITUTION: H2 is fed near the entrance of a deoxidizer catalyst 2. The air amount is measured by a suction air amount sensor 5 of an engine E to make the H<sub>2</sub> to feed at the same level with the NOx in the exhaust gas. The NOx density in the exhaust gas is found by an NOx sensor 6, and after the NOx flow is calculated from the outputs of both sensors 5 and 6 in a controller 7, the fuel flow led in a reformer catalyst converter, and the reformer catalyst converter temperature by an exhaust gas flow dividing valve 11, and also an air valve 12 for reforming in the system to carry out a partial oxidization, are controlled in order to generate the H<sub>2</sub> corresponding to the NOx flow.

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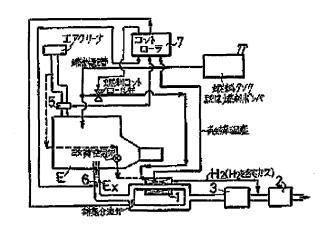
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#### (54) 【発明の名称 】 内燃機関の窒素酸化物低減装置

#### (57)【慶約】

【目的】 リーンバーンエンジンやディーゼルエンジン 等において当該エンジンの燃費の良さを損なうことなく 排気ガス中の○。の濃度如何を問わずNO。を有効に還 元浄化し得る内燃機関のNO、低減装置を提供する。

【構成】 内燃機関Eの燃焼室で供給燃料の燃焼による 排気中にNO』とO、の存在のもと、排気系統Ex に設 けH。とNOxを接触反応しNOxを浄化する触媒装置 2の入口側に、メタノール又はLPG、天然ガス等の炭 化水素燃料の一部を改質触媒コンバータによってH。を 生成する水素発生装置1からの日。を供給し、排気系統 の消音装置付近における排気低温雰囲気下で該員。によ り前記緋気中のNO、を直接還元浄化して該NO、を効 率良く低減する。



#### 【特許請求の範囲】

【論求項1】 内燃機関の燃焼室で燃料供給装置より供 給された燃料の燃焼による排気中に窒素酸化物と酸素ガ スの存在のもと、俳気系統内で水素ガスと窒素酸化物を **鮭媒反応させ、窒素ガスと水に分解するための触媒装置** を設けると共に、該触媒装置の入口側にメタノール又は LPG、天然ガスなどの炭化水素燃料の一部を改賀触媒 コンバータによって水素を生成する水素発生装置を設 け、水素ガスを供給可能に構成し、排気系統の消音装置 付近における排気低温雰囲気下で該水素発生装置からの 10 水素ガスにより前記緋気中の窒素酸化物を直接還元浄化 して該窒素酸化物を低減するようにしたことを特徴とす る内燃機関の窒素酸化物低減装置。

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#### 【発明の詳細な説明】

#### [0001]

【産業上の利用分野】本発明は、内燃機関の窒素酸化物 低減装置に係り、特に、希薄混合気を使用し、燃料消費 向上をめざす、いわゆるリーンバーンエンジンやディー ゼルエンジン、その他の水素エンジン等において、当該 エンジンの燃費の良さを損なうことなく、緋気中の酸素 20 -ガス(以下〇。と称す)の濃度如何を問わず窒素酸化物 (以下NO、と称す)を有効に還元浄化しうるリーンN 〇、触媒排気浄化システムに関する。

#### [0002]

【従来の技術】内燃機関、主としてビストン機関におい で排気の窒素酸化物(以下NO、と称す)の低減方法に は、従来、

- ② 三元触媒によるNO。低減法
- ② 超希薄空燃比の利用
- 関平1-139145号公報》

の三つが考えられている。しかしながら、①の方法はエ ンジンに供給される燃料と空気の重量比が約14.5、 即ち理論空燃比でなければならない。もし理論空燃此よ り燃料が希薄な空燃比を使用するとNO、は低減しな い。しかるに燃料消費の経済性を考えると図2に示すよ うに理論型燃比より希薄側でエンジンを運転した方が燃 料消費率が少なく、効率が良いことが知られている。

【0003】次に②はいわゆるリーンバーンエンジンに よってNO、低減と燃費低減を両立させようとするもの 40 -である。しかし、NO、を十分低減できる空燃比を使お うとすれば、燃焼の失火限界に近づき、エンジンの燃費 が悪くなるばかりでなく、運転が荒れ、ドライバビリテ すも悪くなる。これを防止するためシリンダ内の空気流 れに乱れや流遠増加を計り、燃焼速度を速くして失火限 界をより希薄域になるように改良しようとするものがあ る。しかし、空気乱れや流遠増加を過度に行うと、かえ って着火時の火炎核形成や燃焼初期の火炎伝播が妨げら れるため、この方法による失火限界の鉱大には限界があ

傍のみ着火に適した濃複合気とする方法もあるが、図3 に示すように失火限界がより希薄側に移ると、発生NO 、も破線で示したように、減少する割合が少なくなるの で大きな効果は期待できない。

【0004】@は上記@の欠点を縋ろため、失火服界よ りやや理論空燃比に近い燃料消費率最低点付近を使って 運転し、やや低減不足のNO。はゼオライト系リーンN ○、触媒で浄化しようとするものである。この方法は燃 費の良いシステムになる可能性がある。しかしながら、 とのリーンNO、触媒は、排気中に大量のO、存在下で NO。を還元することになり、温度条件などが厳しく、 現状では充分な触媒のNO、浄化率と耐久健が両立しに くいといった実用上解決すべき問題がある。以上のよう にエンジンの燃料消費率を極力小さくできる空燃比を使 いながらNO。を充分低減する方法にはいずれも実用上 の問題が多い。

【0005】ととろでリーンバーンエンジンでもディー ゼルエンジンでも鎌気中に過剰〇、を含むことは基本的 に同じであるが、このエンジンの緋気は、緋気中にO。 を含み、希薄混合気を使うほどO、濃度は大きくなる。 とのようなO,を含む嫌気中のNO.還元浄化を行う触 娘をリーンNO、鮭媒といい、貴金属系、例えばゼオラ イト系の触媒が使われることが多い。このリーンNO。 触媒では、NO』巻化率と温度との関係が図4に示すよ うになっている。そして、350℃以上の高温域は、主 としてHC-NO〟の反応である。250~350℃以 下の低温域は、NO、のH。による還元反応となり、N O。の浄化が可能である。

【0006】しかし、リーンNO、触媒は、エンジンの ③ リーンNO、触媒によるNO、低減法(例えば、特 30 排気マニホールド付近に設置されるので、排気温度が最 高800~900℃にも達し、かつリーンバーンエンジ ンの排気は空燃比が理論空燃比より蓄薄側を使うので、 緋気中に目、は殆ど存在しない。従って、従来、低温側 の特性は、利用不可能な領域であった。

### [0007]

【発明が解決しようとする課題】本発明の目的は、上記 従来の種々の問題を解決するもので、リーンバーンエン ジン又は鴬に〇。(空気)過剰側で運転されるディーゼ ルエンジンの排気中にNO〟とO」の共存のもとでリー ンバーンエンジンまたはディーゼルエンジンの燃費の良 さを損なうことなく、嫌気中の〇」の態度如何を問わず NO。を有効に還元浄化する鎌気浄化システムすなわ ち、NO、の放出畳を抑制し得る内燃機関のNO、低減 装置を提供しようとするものである。

#### [0008]

【課題を解決するための手段】本発明の内燃機関のNO 🗴 低減装置は、内燃機関の燃焼室で燃料供給装置より供 給された燃料の燃焼による排気中にNO。とO。の存在 のもと、俳気系統内でH。とNO、を触媒反応させNO る。また、シリンダ内の空燃比分布を調整して点火栓近 50 、を浄化するための無線装置を設けると共に、該触線装 3

置の入口側にメタノール又はLPG、天然ガス等の炭化 水素燃料の一部を改質触媒コンバータによって水素を発 生する水素発生装置を設けて且」を供給可能に構成し、 鎌気系統の消音装置付近における鎌気低温雰囲気下で該 水素発生装置からの月。により前記排気中のNO』を直 接還元浄化して該NO、を低減するようにした構成であ る。

[00009]

【作用効果】上記楼成からなる本発明の内燃機関のNO 、低減装置は、以下の作用を奏する。

【①①10】すなわち、本発明者等が案出した本発明の 内燃機関のNO。低減装置は、図1に示すような構成と することによって、内燃機関の燃焼室で供給燃料の燃焼 による鎌気中にNO、とO。の存在のもと、耳。とNO 。を接触反応させ、窒素ガスと水に分解する排気系統に 設けた触媒装置の入口側にメタノール又はLPG、天然 ガスなどの炭化水素燃料の一部を改置触媒コンバータに 導きH、を生成する水素発生装置からのH」を供給し、 緋気系統の消音装置付近における緋気低温雰囲気下で該 月。により前記排気中のNO、を効率良く的確に直接還 20 m 元浄化して該NO。を低減する作用効果を奏する。この ため、本発明の内然機関のNO、低減装置は、エンジン の使用空燃比が理論空燃比より過濃側、理論空燃比、理 論空燃化より需藤側と排気中の〇、の存在又は〇、の濃 度に関係なくNO、を触媒によって低減できるのでエン\*

CH<sub>8</sub> OH + Air →

【0017】となる。

【① 0 1 8 】 3 ) 触媒にCu - MnまたはCu - Znを 用い、メタノールに水蒸気を加えるかまたは空気やメタ ノール水を加え水蒸気改質を行う。温度は250℃程度※30

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

【0020】となる。

【0021】また、LPG、天然ガスなどの炭化水素燃 料を使うエンジンにあっては、触媒としてNi、CO、 Rhを使い、温度300~800℃で改質する。この炭 化水素燃料の場合には、水蒸気や空気や水タンクからの★

$$HC + H_2O \rightarrow H_2 + CH_2$$
 $HC + H_2O \rightarrow H_2 + CO$ 
 $HC + Air \rightarrow H_2 + CO$ 
 $HC + 排気 \rightarrow H_2 + CO$ 

【0023】となる。

【0024】また、本実施側の内燃機関のNO。低減等 置は、前記継気系統の継気管に装備するNOx センサ6 と吸入空気置センサ5の出力からNO、液置を算出し、 常に適正な月。量を決定し前記水素発生装置としての改 質触媒コンバータを加熱するエンジン排気流置又は部分 50 の内燃機関における運転条件を検知できるセンサを具備

\* ジン(自動車)性能上、燃費上NO、低減条件を考慮せ ずに最適値を選ぶことができる有利さを持たせ得る。

[0011]

【実施例】実施例における水素発生装置はエンジンに使 用する燃料によって改質触媒コンバータが次のように分 類される。

【0012】すなわち、メタノールを燃料とするエンジ ンにあっては

1) Pd、Pt. Cu/Cr/N:等の遷移金厩触媒を 10 用い、メタノールを鲱気によって加熱蒸発させたガス を、この触媒に導きH1、を生成する。触媒入口ガス温度 は300℃程度が最良であって、この時の反応は

[0013]

[{{k}}]

$$CH_3OH \rightarrow CO + 2H_2$$

【0014】となる。

【0015】2)メタノール蒸気に空気を復合させ、C  $u - N_1 - C_1 / P$ ルミナ触媒によってメタノールの一 部を部分酸化させ、H』を生成する。温度は400℃~ 500℃が適当であり、メタノールに混入させる空気流 置をコントロールし、温度を保つようにする。この場合 の反応は、

[0016]

[(12]

+ CO + H<sub>2</sub> O  $H_2$ 

※が適当で、反応は

[0019]

[化3]

★水を加えて改質を行う。(触媒により温度が異なる。低 温ではメタンが多く、高温ではCOが多い)。反応とし Tià.

[0.022]

【化4】

300~500°C + CO2

+ CO2 3000

8000

7000

(EGR改質)

酸化を行う場合の空気置および改質燃料量を制御する機 成とすることもできる。

【①025】さらに、本実施例の内燃機関のNO。低減 装置は、当該内燃機関の回転数、吸気管負圧、吸気絞り 弁開度又は燃料供給装置としての噴射ポンプの噴射置等 し当該センサの出力からNO、流置を予測演算し前記水 **素発生装置の改賀触媒コンバータに供給する燃料量をコ** ントロールする学習制御方式にした構成とすることもで きる。

【0026】しかも、本実施例の内燃機関のNO。低減 接置は、前記触媒装置の入口側においてH』と排気の復 |台を均一にするため、ミキサーを具備したり、または、 緋気系統の消音装置を有効利用する構成とすることもで きる。

【0027】詳述すれば、本実施例の内燃機関のNO、 低減装置は、前記従来の問題を解消するために案出され たものでその基本構成図を図しに示す。すなわち、本実 施例の第1のポイントは、この日、還元が鎌気低温側で エンジンEの全運転範圍において使用することである。 第2のポイントは、低温側の利用を可能にするため構成 システム中にH、発生器1を組み込むことである。第3 のポイントは、エンジン目の運転状態又は緋気中のNO 、量によってH。発生器 1 を制御し、常に緋気中NO。 とモルで当置程度又は過剰の日、が供給できるようにす るととである。

【① ①28】 還元触媒2は高温にさらされるとH。が〇 、と反応し頁。−NO<sub>x</sub>の選択性が失われるので、35 ① \*C以上にさらされることのないよう消音器3の付近に 配置する。そして、本実施例は、燃料配管から分岐し、 流量コントロール弁を介して日、発生器としての改質態 娘コンバータに燃料を導入改質してH。を発生させる。 | F| 。は、還元触媒2の入口付近に供給する。供給する日 **、は、緋気中のNO、とモルで当畳程度にするためにエ** ンジンEの吸入空気量センサ5によって空気量を測定 し、排気中のNO、濃度をNO、センサ6によってを求 30 め、コントローラ?で両をンサ5、6の出力からNO<sub>x</sub> 流量を演算した上で、NO。流量に対応する目。を発生 させるため改貨触媒コンバータに導入する燃料流量や、 俳気分流弁による改質触媒コンバータ温度、部分酸化を 行うものでは改賢用型気弁の制御を行う構成である。

【0029】図5において、 横軸は、 NO、 に対する日 ,の供給比、緩軸は、NO』の還元率(浄化率)を示。 す。NO、に対して等置の(モル)H。を供給すれば、 もしNO、とH。が完全に混合するものとすればNO。 はすべて還元浄化される(理論値)。しかし実際には完 40 全混合されないので還元率は実験値のようになる。理論 より実験値の方が浄化率が良くなっている部分がある。 が、これは鎌気中の水蒸気が貴金属系触媒上で分解し其 ,に変換していることによる。従って、供給したH』よ り多くの日。がNO、と反応する。

【0030】その他の実施例としては、月、による還元 浄化を行うNO。低減装置において改資無媒コンバータ の入口側にH。と鲱気とを混合ミキシングするミキサー を設置する機能とすることができる。また本実施例のそ の他のNO、浄化装置である水素発生器および触媒装置 50 ている。図6中、15はエンジンE、への空気量を測定

は、それぞれ好適な作動温度範囲を持つため、内燃機関 の排気系統において水素発生器を排気マニホールドの出 口に設置した酸化無媒の後段に、また還元無媒は排気が 膨張し温度が200℃以下に下がるマフラー内。 あるい

はその下流に設置することができる。

【0031】さらに、その他の実施例としては、水素発 生器の月」を供給してO。共存下のエンジン俳気中のN O. を還元券化するNO. 低減装置において、エンジン の排気マニホールド付近に酸化鮭媒、三元鮭媒、排気リ アクタ等のHC.COを酸化する手段を持ち、かつリー ンNO、触媒としての改質触媒コンバータにPt-ゼオ ライト系触媒を用いる構成とすることができる。また、 改質触媒コンバータに消音効果を持たせ改質無媒コンバ ータと緋気マフラーを一体化構成とすることができる。 【0032】しかも、H〟によるNO〟還元を行うNO 、浄化装置において、ディーゼル機関用として改賀触媒 コンバータの上流にスートトラッパ。未燃焼生成物酸化 手段を設置した構成とすることができる。また、本実施 例において、内燃機関はガソリンエンジン、ディーゼル 20 エンジンの他、水素エンジンでも良く、これらのNOx 低減装置に有効に適用し得る。この水素エンジンの場合 は、水素発生装置が必要でなく、燃料としてのH。をコ ントローラを介してバイバス的に供給することにより適 用することができる。

[0033]

【第1実施例】エンジン排気置11のリーンバーンエン ジンに本発明のシステムを適用する第1実施例を図6に 示す。第1実施例のエンジンE、は、アイドル時の空気 過剰率入=0.95~1.0(理論空燃比よりやや過濃 側が理論型燃比)各回転数の全負荷時および急激加速時 はえ=0.8~1.0(過滤側)、これ以外の運転条件  $は\lambda = 1$ .  $2 \sim 1$ . 8の番藤側で運転するエンジンE、 である。従って、俳気中の〇」は、0~10%程度まで 変化する。緋気系統B、は、緋気マニホールF8の出口 に酸化触媒9を設置し、HC、CO等の不完全燃練生成 物を酸化し浄化する樺成である。さらに、消音器として のマフラー13の下流側に還元触媒12を配置する。還 元触媒 12の入口にはH。と緋気との混合を均一化する ためミキサー10が設けられている。

【0034】H。発生器11は、図7、図8に示すよう に改賀触媒14を用いた水電解目、発生器である。 【0035】水素発生器11は分岐された鎌気管内にコ

イル状のインナーコアを形成し、インナーコアの一端に はメタノールを噴射する電磁燃料噴射弁が設けてあり、 他端はミキザーに導かれている。インナーコアの入口付 近はメタノールを蒸発させるための多孔セラミックが充 鎮してあり、その後にはペレット状の改質触媒が詰まっ ている。(モノリス状の触媒を使うときはインナーコア をコイル状から直線状に変更する。) 触媒はPdを使っ

する吸入空気量センサで、16は俳気中のNO、濃度を 測定するNO、センサである。

【0036】本第1実施例の場合、NO、とモルで当置のH。を必要とするので、エンジンE、の排気中のNO、機度にもよるが、50km/hの車速のとき0.31/min程度のH。を必要とする。このH。は燃料の一部を改質して供給されるものであるが、それぞれの運転条件下における消費H。が走行燃費に及ぼす影響は1~2%以下であり、リーンバーンエンジンを使う燃費低減メリット15~20%に此べれば無視できる程度であり、リーンバーンエンジンの低燃費特性を損なうことがない。【0037】また、H。発生に要するメタノールは、50km/h走行で0.151/min(蒸気)程度である。

【①①38】以上のように本第1実施例は、少量の無料をH。発生器11において改質して還元無媒12の低温側特性を利用して、H。-NO、還元を行うので、エンジンE、の運転空気過剰率入に無関係にNO、の低減が計れる実用上有意義なリーンバーンNO、低減ンステム 20である。また、H。と共に副生するCOはシフト反応【①①39】

#### [化5]

CO → H,O → H₂ ← CO₂ 【0040】でH,に変換するか、またはPd膜により H₂ とCOとに分離し、高純度なH。として還元触媒1 2の前方に供給する方法もある。しかし、副生するCO は微量であり、そのまま還元剤として還元触媒12の中で働くことができ、COを放出することはない。

#### [0041]

【第2実施例】第2実施例は、空調用、発電用等に使うガスエンジンの場合である。燃料は天然ガスの場合を示す。このような目的の定置用エンジンは自動車用と異なり、一定回転数、一定負荷で運転される。従って、改質触媒コンバータの温度は一定に保ち易い。第2実施例の機成は図9に示すように前記第1実施例とほぼ同一であるので、同一部分は同一符合を付して説明を省略する。【0042】水素発生器に供給する燃料は第1実施例と異なり、天然ガスであり、空気と混合して供給する必要な日。を確保するため、空気、天然ガスとも調整弁により、大然ガスであり、空気と混合して供給する必要な日。を確保するため、空気、天然ガスとも調整弁により、でコントロールする。コントロールは、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同じ様で、前記第1実施例とほぼ同様の作用効果を奏する。

### [0043]

【第3実施例】前記各実施例において、燃料の一部を改質して日、を発生させる装置とゼオライト系触媒を組合せ、NO、を還元浄化するエンジンのNO、低減失置は、日、の供給条件、内容によってNO、低減性能に大きな差異を生じることが分かってきた。図10に示すように、NO、、O、を含むエンジンの排気を触媒に流

し、改質触媒コンバータの上流から日。を供給した場合のNO、浄化率を図11に示す。図11において情報はNO、に対する日、の供給割合を示し、1.0は、NO、と日、が当重の場合である。縦軸は還元によってNO、が浄化される割合であって、1.0はNO、がすべて

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【0044】図10に示す改質触媒コンバータ60内に、図12に示すベレットタイプの触媒61が入っている場合は図14から分かるように高い浄化率を示す。図1013に示したモノリスタイプの触媒62にすると、同じ日。供給置であっても浄化率は低下する。

巻化されてしまうことを示す。

【① 0.4.5】図12に示したペレットタイプの触媒61は、入口で日。と俳気ガスとが十分混合せず、H。に濃度分布があっても迷路のようなペレットの隙間をガスが直通して行く過程で十分混合し、日。と俳気ガスが均一化される。

【0046】一方、図13に示したモノリスタイプの無 媒62は、断面 "蜂の巣" 状の孔をが多数有しており、一個の孔はガス流れの方向に独立しているので、入口で 日。に分布があれば途中で互いに隣り合う流路内のガス が混合しにくい。実際の実験によれば、排気管の太さは 章載上の制約から大幅に太くすることは困難でガス流速 は遠く、日。は中央部付近に高濃度領域を作り、モノリス 周辺部には日。がほとんど供給されない不都合を生じている。従って、モノリスタイプは、日。の利用率がペレットタイプに比べ低い。

【0047】一方、エンジン緋気システムとして見ると、ベレットタイプは振動によってベレットが互いに擦れ合って粉末化し易いこと、ガスの直通断面積が小さ30 く、通過抵抗が大きく、排圧増大を招き、エンジン性能自身を悪化する欠点がある。従って、触媒にはモノリスタイプを使うことが整ましいが、この場合には耳。の供給に工夫が必要になる。

【① 048】そこで、第3実施例は、モノリスタイプの 触媒を使いベレットタイプより優れたNO、巻化率を得 るよう日、の供給を均一混合する構成上簡素な装置から 成る。すなわち、混合装置69としての日、噴出ノズル 63の基本的構造を図14、図15に示す。挿入された 日、噴出ノズル63は、中空円筒形状で、排気の流れ方 向にし字状に曲がっており、放射状に複数の噴出孔64 を有する。放射状の噴出孔64は、4~6個が適当で、 1列又は復数列設けられている。(図14では噴出孔が 3列配設されている)。

【0049】嗜出ノズル63の挿入管外径はと排気管65の内径DとははがDの20%以上必要で、また大きくすると流路の抵抗が大きくなるので図16に示すように排気管65の一部を断面拡大形成する。又、噴出ノズル63から改質触媒コンバータ60までの距離しはDの少なくとも2倍以上を必要とし、10倍以上大きくしても50改善効果は少ない。複合装置は、上述の他に、構成を図

17. 図18に示すようにすることができる。すなわ ち、H,を纔鉢させる部分は、小径のH,噴出ノズル6 6とこれより大径で壁部に複数の噴出孔67を設けた有 艦筒68とから成るほぼ2重管状に構成されている。 噴 出した月。は、まず、月。噴出ノズル66に郷圧の動圧 によって流入する排気と混合し、有底筒68の内筒から 外筒に噴出し、内外筒の間を流れる排気により更に混合 する。このように2段階の舞台過程を経るのでほぼ買。 と排気が完全に均一混合することができる。

【0050】内外筒の大きさ(直径、または断面積)は 10 -復合に大きく影響し、内筒が小さいとほとんどの排気は 外筒を流れ、十分動圧を利用できない。図17. 図18 に於いて内外筒の直径此はD/a (外筒/内筒)は3~ 1. 7程度が有効で2付近が最良である。

【①①51】上記楼成からなる第3実施例は、混合が良 好となり、モノリスタイプであってもペレットタイプ同 様の浄化率を得ることができる。同一浄化率において供 給H、畳を30~60%節約することができるので、H **、発生に要する燃料を少なくでき、エンジンの出力や燃** 養への影響を軽減できる。

【0052】倒えば、1.6!のリーンバーンガソリン エンジンにおいて通常の運転域代表点で評価すると、エ ンジン回転数2000mpm、トルク40Nm、この時 のNOx 放出量(). 441/min. このNOx を用x 還元で浄化するのに要するH、流量は、0.661/m in。(). 661/minのH, を発生させるのにH, 発生器への燃料は(). 331/minの燃料蒸気になる (メタノールの場合)。

【0053】D/d=2である図17、図18に示す鏃 等量の(). 441/m・n程度で済み、燃料は(). 22 | / m | n の蒸気0 | 2 2 1 / m | n の蒸気に低下す| る。即ち0.11!/minの節約となる。 [0.054]

【第4実施例】前記実施例においてゼオライト系触媒を 用い、水素発生器によって水素を発生させ、目。をゼオ ライト系触媒の入口に供給しHzによるNOx 還元を行 えば排気中に高濃度の0.が存在していても大きなNO 、浄化率が得られる。

【① 0.5.5 】しかし、従来のN O、触媒、例えば三元絵 40 -媒、Cu - ゼオライト系触媒に比べると低温の反応であ って、従来の触媒がSV値(通過ガス流置!/hrと触 媒体積1の比)50,000~100,000を使って いるのに比べると反応速度の関係からより小さなSV (例えば10、000~60,000)を使わなくては ならない。このシステムを車載する場合、本システムの 改賀触媒コンバータは入口ガス温度から排気系統の下。 癒。例えば俳気マフラー付近になる。しかるに車輌に於 いては車輌構造上SV値の大きい(コンバータの大きさ の大きい)改賢触媒コンバータを設置する場所になって 50 ジンの緋気にH,を混合してNO、低減のリーンNO、

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おり、すべての車輛へは適用し難い。

【①①56】本第4実施例は、改質触媒コンバータの設 置を容易にするため、リーンNO、触媒をマフラーに内 蔵させコンパクト化を計るためのマフラー構造およびマ フラーに触媒を内蔵させても温度条件からNO。浄化を 可能とするものである。

【0057】すなわち、第4実施例の構成は、図20、 図21に示すように、鎌気マフラー80にリーンNO。 **触媒82を内蔵させるとNO、コンバータと、排気マフ** ラーを直列に配置することなく片方で済むため、配置ス ベース的に極めて有利となる。図20.図21に排気マ プラー80にモノリス触媒82 (Ptーゼオライト系) を内蔵した消音効果を持たせた改質触媒コンバータ83 を示す。

【0058】改賀鮭嵁コンバータ83の上漉よりH,を 混入混合された排気が矢印方向より流入し、ミキシング プレート84に衝突し、このミキシングプレート84の 大小複数の流通孔85を通過して緋気と耳。が十分混合 しながらモノリス触媒82に添入する。ミキシングプレ 20 ート84には排気流速最大になる中心部に流通孔85が 設けられていないので、H.がモノリス中心部に集中す ることはない。ミキシングプレート84の流通孔85 は、大小それぞれ直径を異にして複数配列されているの。 で通過流速が異なり、ガスの鍵撑が起こると共に干渉に よって消音効果を奏する。

【0059】ととろで、排気マフラーはエンジン排気系 統の最後尾に配置されるのが一般的で、鎌気マフラーの 入口ガス温度は途中で冷却されるので低くなる。入口温 度が最も高いエンジンの最高回転数最大馬力時でも15 置によって複合促進を行えば、H. の供給置はNO、と 30 0~200℃であり、通常使用頻度の高い運転条件では 100~150℃程度である。

> 【0060】従来の三元触媒やCu-ゼオライト系のリ ーンNO、鮭媒では300~400℃以上でないと十分 な反応が期待できないからマフラー内に触媒を内蔵させ ることはできない。前記実施例において、H,による墨 元を行えば低温で浄化できることを示したが、温度は1 50~300℃程度であって緋気マプラーの入口温度と 比べればやや高い温度範囲にある。

> 【0061】本発明者等は、〇、共存下でH、を供給す るNO、低減触媒の活性について触媒成分として何を選 定するべきかを種々実験的に検討した。その結果、P. d. Rhは活性が全くなく、Cuは活性が悪く、Ptが 高い活性を示すことを見出した。ただし、Ptは高分散 である必要があり、そのためには高比表面績(少なくと も100m<sup>4</sup> / g以上) を育するアルミナ、シリカ、ゼ オライト等の組体が必要である。

> 【0062】更に、本発明者等は、NO、低減のリーン NO、鮭媒および貝、混合以前に行うべき前処理につい て種々に検討を行った。その結果を図19に示す。エン

触媒(Pt系)に導くと図19中、曲線Bに示すように 活性の最高点は250℃付近にある。

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【0063】アフターバーナ、リアクタ、三元触媒、酸化触媒等をエンジンマニホールド付近に設け、CO、HCを酸化し予め低減除去した後にH。を供給しNO。低減の改質無媒コンバータに導くと図19中曲線Aに示すように活性温度が低温側にシフトし、100~150℃で高い活性を示すことを新たに見出した。

【① 0 6 4 】との温度は、排気マフラーの入口温度と一致し、排気マフラー8 0 内に P t ーゼオライト系の還元 10 触媒 8 0 を内蔵することにより初めて可能ならしめた。 更に、HC、COを除去した後にリーンNO、触媒によるNO、浄化を行った方が浄化率も改善でき、HC-O、の不完全な反応から触媒上にススを形成することもない実用上優れた作用効果を奏する。

【0065】更にモノリス触媒82の後に干渉チューブ E×1を設置することにより消音効果をより良好にしている。図22は図20、図21と同様の作用効果を奏するもので、ミキサー部の形態を前記ミキシングプレートと異にし、中空筒状部材であるミキシングバイブ86と 20 した点が異なる。上記構成からなる第4実施例は、改質無媒コンバータ83と排気マフラー80が一体化構成とすることができるので、コンバクトとなり卓載性が良好となる実用的効果を奏すると共に、全運転範囲で高いNO、浄化率を維持できる優れた効果を奏する。

#### 【図面の簡単な説明】

【図1】本発明の実施例の基本構成を示す構成図

【図2】空燃比と燃料経済性の関係を示す線図

【図3】リーンバーンエンジンの熱資とNO〟の関係を 示す線図

【図4】リーンNO、触媒の特性を示す線図

【図5】 H、供給率とNO、浄化率の関係を示す線図

【図6】本発明の第1実施例装置の概要を示す構成図

【図7】第1実施例装置におけるH。発生器の断面図

【図8】第1実施例装置におけるその他の月、発生器の

要部を拡大して示す構成図

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\*【図9】本発明の第2実施例装置の概要を示す構成図

【図10】本発明の第3実施例装置の概要を示す構成図

【図11】第3実施例装置に関してNO、浄化率の関係 を示す線図

【図12】第3実施例装置に関してペレットタイプの触 媒構成を示す概要図

【図13】第3実施例装置に関してモノリスタイプの触 媒構成を示す概要図

【図 1 4 】本発明の第3実施例装置の概要を示す縦断面

【図15】本発明の第3実施例装置の概要を示す機断面図

【図16】本発明の第3実施例装置の概要を示す概要図

【図17】本発明の第3実施例装置のその他の例を示す 縦断面図

【図18】本発明の第3実施例装置のその他の例を示す 満断面図

【図19】本発明の第4実施例に関してNO。浄化率状 視を示す線図

6 【図20】本発明の第4実施例装置の概要を示す縦断面図

【図21】本発明の第4実施例装置の概要を示す情断面図

【図22】本発明の第4実施例装置のその他の構成を示す縦断面図

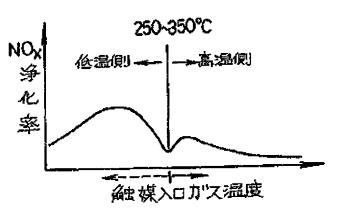
【符号の説明】

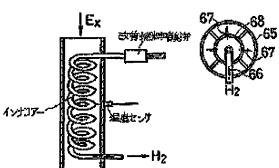
D. D <sub>1</sub>	حمل عمل على علي
1. 11	H,発生器
3.13,80	消音器
12.60	還元触媒
9	酸化触媒
5	吸入空気置センサ
6	NOx センサ
7	コントロール電源

[図7]

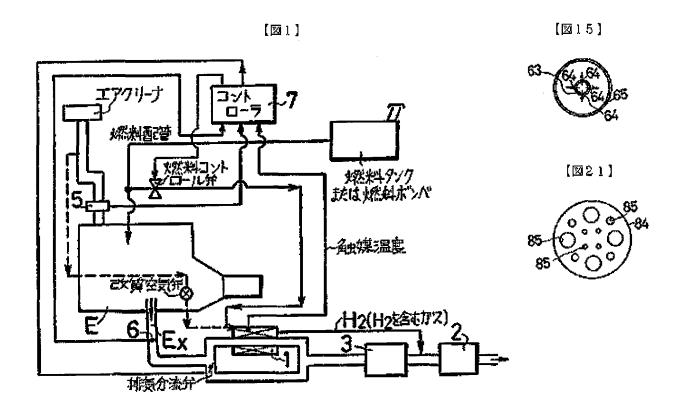
10 ミキサー

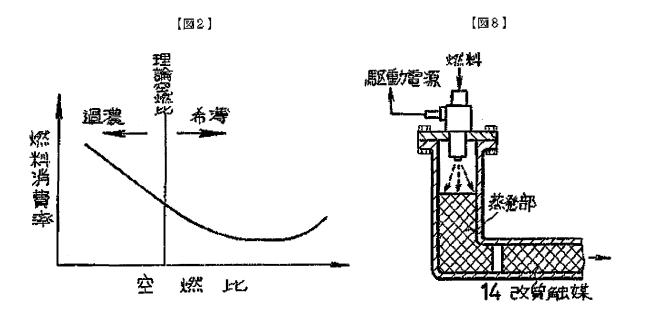
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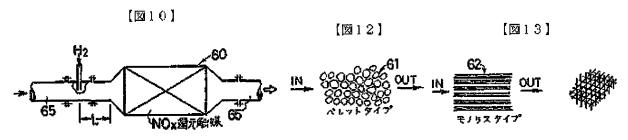


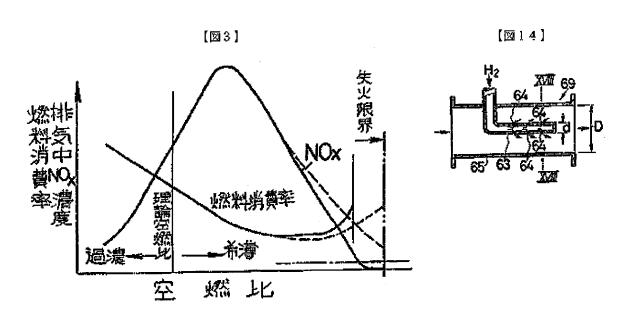


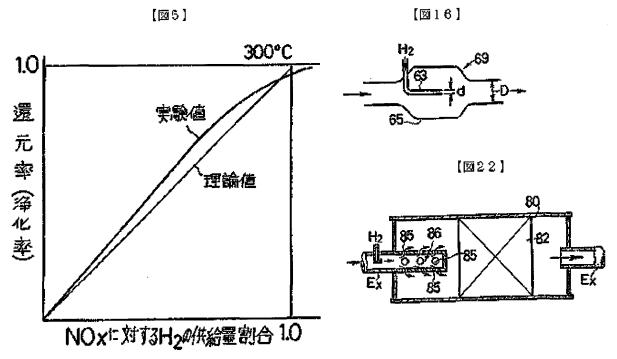
[2018]

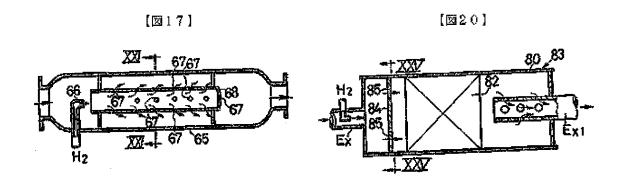




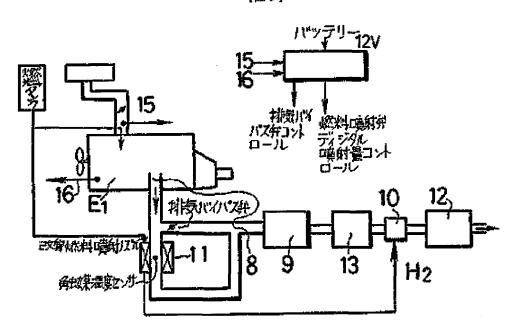




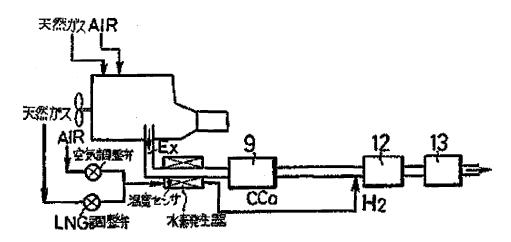




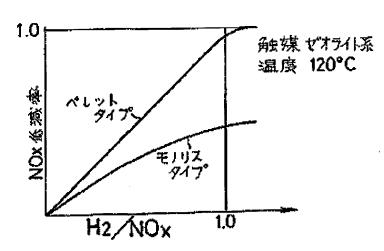
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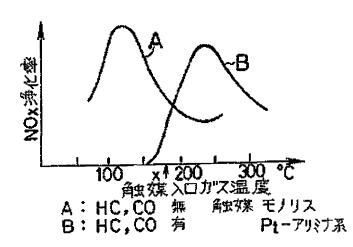
[29]







[図19]



フロントページの続き

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PURPOSE: To deoxidize and purify the NOx in the exhaust gas

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YOKOTA KOJI

NAKANISHI KIYOSHI

# (54) NITROGEN OXIDE REDUCING DEVICE FOR INTERNAL COMBUSTION ENGINE

### (57)Abstract:

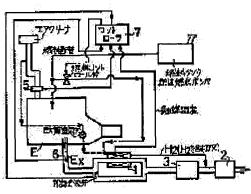
directly by the H2 from a hydrogen generator under the exhaust gas low temperature ambiance so as to reduce the NOx, by composing the system to make a part of a hydrocarbon fuel converted into a hydrogen gas to feed by a reformer catalyst converter. CONSTITUTION: H2 is fed near the entrance of a deoxidizer catalyst 2. The air amount is measured by a suction air amount sensor 5 of an engine E to make the H2 to feed at the same level with the NOx in the exhaust gas. The NOx density in the exhaust gas is found by an NOx sensor 6, and after the NOx flow is calculated from the outputs of both sensors 5 and 6 in a controller 7, the fuel flow led in a reformer

catalyst converter, and the reformer catalyst converter temperature by

reforming in the system to carry out a partial oxidization, are controlled

an exhaust gas flow dividing valve 11, and also an air valve 12 for

in order to generate the H2 corresponding to the NOx flow.



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- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **CLAIMS**

### [Claim(s)]

[Claim 1]Both that it is characterized by comprising the following to an entrance side of this catalyst device Methanol or LPG, A hydrogen generator which generates hydrogen by a reforming catalyst converter for some hydrocarbon fuel, such as natural gas, is provided, A nitrogen-oxides reduction device of an internal-combustion engine constituting hydrogen gas so that supply is possible, carrying out direct reduction purification of the nitrogen oxides under said exhaust air with hydrogen gas from this hydrogen generator under an exhaust air low temperature atmosphere in near the silencer of an exhaust system, and reducing these nitrogen oxides.

A basis of existence of nitrogen oxides and oxygen gas during exhaust air by combustion of fuel supplied from a fuel supply system in a combustion chamber of an internal-combustion engine.

A catalyst device for carrying out catalytic reaction of hydrogen gas and the nitrogen oxides inside, and decomposing into nitrogen gas and water.

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- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **DETAILED DESCRIPTION**

# [Detailed Description of the Invention]

### [0001]

[Industrial Application]In what is called the lean burn engine and the diesel power plant, other hydrogen fueled engines, etc. which this invention requires for the nitrogen-oxides reduction device of an internal-combustion engine, and use a lean mixture and aim at the improvement in fuel consumption especially, without it spoils the goodness of the fuel consumption of the engine concerned -- the concentration of the oxygen gas (O<sub>2</sub> is called below) under exhaust air -- it is related with the Lean NO<sub>X</sub> catalyst exhaust gas cleaning system which can carry out reduction purifying of the nitrogen oxides (NO<sub>X</sub> is called below) effectively regardless of how.

# [0002]

[Description of the Prior Art]In a piston engine, as an internal-combustion engine and the Lord, to the reducing method of the nitrogen oxides ( $NO_X$  is called below) of exhaust air. The  $NO_X$  decreasing method by the use \*\* Lean  $NO_X$  catalyst of the  $NO_X$  decreasing method \*\* super-rarefaction air-fuel ratio by the former and \*\* three way component catalyst (for example, JP,1-139145,A)

Three \*\* are considered. However, the weight ratio of the fuel in which the method of \*\* is supplied to an engine, and air must be about 14.5, i.e., theoretical air fuel ratio. If fuel uses a thin air-fuel ratio from theoretical air fuel ratio, NO<sub>X</sub> does not decrease. However, it is known that considering the economical efficiency of fuel consumption specific fuel consumption has few directions which operated the engine by the thin side from theoretical air fuel ratio as shown in drawing 2, and it is efficient.

[0003]Next, \*\* tends to reconcile NO $_X$  reduction and fuel consumption reduction with what is called a lean burn engine. However, if it tries to use the air-fuel ratio which can reduce NO $_X$  enough, it approaches the misfire limit of combustion, and engine fuel consumption not only worsens, but it will be ruined and drivability will worsen. In order to prevent this, disorder and the increase in the rate of flow are measured with the air flow in a cylinder, the rate of combustion is made quick and there are some which are going to improve a misfire limit so that it may become a thin region more. However, since the flame kernel formation at the time of ignition and the flame propagation in early stages of combustion will be barred on the contrary if air disorder and the increase in the rate of flow are performed too much, there is a limit in expansion of the misfire limit by this method. Although there is also the method of making it into the rich mixture which

adjusted the air-fuel ratio distribution in a cylinder and to which only the neighborhood of an ignition plug was suitable for ignition, since the decreasing rate will decrease as the dashed line also showed generating  $NO_X$  if a misfire limit spreads to a thin side more as shown in drawing 3, a big effect is not expectable. [0004]\*\* In order to compensate the fault of the above-mentioned \*\*, it is going to operate using near [slightly near theoretical air fuel ratio] a specific-fuel-consumption minimum score from a misfire limit, and  $NO_X$  in which reduction is a little insufficient tends to purify with a zeolite system Lean  $NO_X$  catalyst. This method may become a fuel-efficient system. However, there is a problem which should be solved practically that  $NO_X$  purifying rate and endurance of catalyst this Lean  $NO_X$  catalyst will return  $NO_X$  under a lot of  $O_2$  existence during exhaust air, severe [a catalyst] temperature conditions etc. and sufficient under the present circumstances can be easily incompatible. The method of reducing  $NO_X$  enough all has many practical problems, using the air-fuel ratio which can make engine specific fuel consumption small as much as possible as mentioned above.

[0005]By the way, although it is fundamentally the same that excess  $O_2$  is included during exhaust air also by the lean burn engine or a diesel power plant,  $O_2$  concentration becomes large, so that exhaust air of this engine uses a lean mixture including  $O_2$  during exhaust air. The catalyst which performs  $NO_X$  reduction purifying under exhaust air containing such  $O_2$  is called Lean  $NO_X$  catalyst, and the catalyst of a preciousmetals system, for example, a zeolite system, is used in many cases. In this Lean  $NO_X$  catalyst, the relation between  $NO_X$  purifying rate and temperature shows drawing 4. And a not less than 350 \*\* pyrosphere is mainly a reaction of  $HC-NO_X$ . A low temperature region 250-350 \*\* or less serves as a reduction reaction by  $H_2$  of  $NO_X$ , and purification of  $NO_X$  is possible for it.

[0006]However, since an exhaust-gas temperature amounts also to a maximum of 800-900 \*\* since a Lean NO<sub>X</sub> catalyst is installed near an engine exhaust manifold, and an air-fuel ratio uses a thin side from theoretical air fuel ratio in exhaust air of a lean burn engine, H<sub>2</sub> hardly exists during exhaust air. Therefore, the characteristic by the side of low temperature was a field which cannot be used conventionally. [0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention is what solves the above-mentioned conventional various problems, Without spoiling the goodness of the fuel consumption of a lean burn engine or a diesel power plant under coexistence of  $NO_X$  and  $O_2$  during exhaust air of a lean burn engine or the diesel power plant always operated by the  $Oover_2$  (air) side, the concentration of  $O_2$  under exhaust air -- it is going to provide  $NO_X$  reduction device of the exhaust gas cleaning system, i.e., the internal-combustion engine which can control the burst size of  $NO_X$ , which carries out reduction purifying of the  $NO_X$  effectively regardless of how.

[8000]

[Means for Solving the Problem] $NO_X$  reduction device of an internal-combustion engine of this invention, A basis of existence of  $NO_X$  and  $O_2$  during exhaust air by combustion of fuel supplied from a fuel supply

system in a combustion chamber of an internal-combustion engine, Form a catalyst device for carrying out catalytic reaction of  $\rm H_2$  and the  $\rm NO_X$  within an exhaust system, and purifying  $\rm NO_X$ , and. Provide a hydrogen generator which generates hydrogen by a reforming catalyst converter for some hydrocarbon fuel, such as methanol or LPG, and natural gas, in an entrance side of this catalyst device, and  $\rm H_2$  is constituted so that supply is possible, It is the composition of carrying out direct reduction purification of the  $\rm NO_X$  under said exhaust air by  $\rm H_2$  from this hydrogen generator under an exhaust air low temperature atmosphere in near the silencer of an exhaust system, and having reduced this  $\rm NO_X$ .

[0009]

[Function and Effect] $NO_X$  reduction device of the internal-combustion engine of this invention which consists of the above-mentioned composition does the following operations so.

[0010]Namely,  $\mathrm{NO}_{\chi}$  reduction device of the internal-combustion engine of this invention which this invention person etc. invented, The basis of the existence of  $\mathrm{NO}_{\chi}$  and  $\mathrm{O}_{2}$  during exhaust air according to combustion of supply fuel in the combustion chamber of an internal-combustion engine by having composition as shown in drawing 1, Carry out the catalytic reaction of  $\mathrm{H}_{2}$  and the  $\mathrm{NO}_{\chi}$ , and to the entrance side of nitrogen gas and the catalyst device formed in the exhaust system decomposed into water Methanol or LPG,  $\mathrm{H}_{2}$  from the hydrogen generator which leads some hydrocarbon fuel, such as natural gas, to a reforming catalyst converter, and generates  $\mathrm{H}_{2}$  is supplied, The operation effect which carries out direct reduction purification of the  $\mathrm{NO}_{\chi}$  under said exhaust air exactly efficiently by this  $\mathrm{H}_{2}$  under the exhaust air low temperature atmosphere in near the silencer of an exhaust system, and reduces this  $\mathrm{NO}_{\chi}$  is done so. For this reason,  $\mathrm{NO}_{\chi}$  reduction device of the internal-combustion engine of this invention, Since an engine operating air-fuel ratio can reduce  $\mathrm{NO}_{\chi}$  according to a catalyst regardless of the concentration of existence of  $\mathrm{O}_{2}$  a thin side and under exhaust air, or  $\mathrm{O}_{2}$  from a rich side, theoretical air fuel ratio, and theoretical air fuel ratio, from theoretical air fuel ratio On engine (car) performance, The profitableness which can choose an optimum value without taking into consideration fuel consumption top  $\mathrm{NO}_{\chi}$  reduction conditions can be given.

[0011]

[Example]A reforming catalyst converter is classified according to the fuel which uses the hydrogen generator in an example for an engine as follows.

[0012]That is, if it is in the engine which uses methanol as fuel, the gas which carried out heating evaporation of the methanol by exhaust air is led to this catalyst using transition metal catalysts, such as 1Pd, Pt, and Cu/Cr/nickel, and H<sub>2</sub> is generated. About 300 \*\* is best and catalyst inlet gas temperature is a reaction at this time. [0013]

[Formula 1]  $C H_3 O H \rightarrow C O + 2 H_2$ 

[0014]It becomes.

[0015]2) Make methanol vapour mix air, according to Cu-nickel-Cr/alumina catalyst, carry out partial

oxidation of some methanol, and generate  $H_2$ . 400 \*\* - 500 \*\* are suitable for temperature, it controls the air flow rate made to mix in methanol, and maintains temperature. The reaction in this case, [0016] [Formula 2]

$$CH_3OH + Air \rightarrow H_2 + CO + H_2O$$

### [0017]It becomes.

[0018]3) Cu-Mn or Cu-Zn is used for a catalyst, and add a steam to methanol, or add air and methanol water, and perform steam reforming. About 250 \*\* is suitable and temperature is a reaction. [0019] [Formula 3]

$$C H_3 O H + H_2 O \rightarrow 3 H_2 + C O_2$$

### [0020]It becomes.

[0021]If it is in the engine using hydrocarbon fuel, such as LPG and natural gas, nickel, CO, and Rh are used as a catalyst and it reforms at the temperature of 300-800 \*\*. In the case of this hydrocarbon fuel, the water from a steam, air, or a water tank is added, and refining is carried out to it. (Temperature changes with catalysts.) There is much methane at low temperature and there is much CO at an elevated temperature. As a reaction, [0022]

$$HC + H_2 O \rightarrow H_2 + CH_4 + CO_2 300~500$$
  $^{\circ}$   $^{\circ}$ 

# [0023]It becomes.

 $[0024]NO_X$  reduction device of the internal-combustion engine of this example,  $NO_X$  flow is computed from the output of the  $NO_X$  sensor 6 with which the exhaust pipe of said exhaust system is equipped, and the suction-air-quantity sensor 5, It can also have composition which controls the air content and the amount of reforming fuel in the case of performing the engine exhaust gas flow or partial oxidation which determines the always proper amount of  $H_2$  and heats the reforming catalyst converter as said hydrogen generator.

flow from the output of the sensor concerned, and is supplied to the reforming catalyst converter of said hydrogen generator.

[0026]And since  $NO_X$  reduction device of the internal-combustion engine of this example makes mixing of

H<sub>2</sub> and exhaust air uniform in the entrance side of said catalyst device, it can possess a mixer or can also consider it as the composition which uses the silencer of an exhaust system effectively. [0027]If it explains in full detail,  $NO_X$  reduction device of the internal-combustion engine of this example was invented in order to solve said conventional problem, and shows drawing 1 the basic constitution figure. That is, the 1st point of this example is that this H<sub>2</sub> reduction uses it in the whole drive range of the engine E by the exhaust air low temperature side. The 2nd point is incorporating the H<sub>2</sub> generator 1 into a constitution system in order to enable use by the side of low temperature. The 3rd point is controlling the H<sub>2</sub> generator 1 by the operational status of the engine E, or the amount of NO<sub>x</sub> under exhaust air, and enabling it to always supply an equivalent grade or superfluous  ${\rm H_2}$  by  ${\rm NO_X}$  and a mol during exhaust air. [0028]Since H<sub>2</sub> will react to O<sub>2</sub> and the selectivity of H<sub>2</sub>-NO<sub>x</sub> will be lost if exposed to an elevated temperature, the reduction catalyst 2 is arranged near the silencer 3 so that it may not be exposed to not less than 350 \*\*. And this example branches from fuel piping, carries out introductory reforming of the fuel via a flow control valve at the reforming catalyst converter as an  $H_2$  generator, and generates  $H_2$ .  $H_2$  is supplied near the entrance of the reduction catalyst 2. In order to make  $H_2$  to supply into an equivalent grade by  $NO_X$  and the mol under exhaust air, an air content is measured by the suction-air-quantity sensor 5 of the engine E, boil  $NO_X$  concentration under exhaust air  $NO_X$  sensor 6, after asking for \*\*\*\* and calculating  $NO_X$  flow from the output of both the sensors 5 and 6 by the controller 7, It is the composition which controls the air valve for refining by the fuel flow introduced into a reforming catalyst converter in order to generate H<sub>2</sub> corresponding to NO<sub>v</sub> flow, and the thing which performs reforming catalyst converter temperature by an exhaust air flow dividing valve, and partial oxidation. [0029]In drawing 5, the delivery late of  $H_2$  [ as opposed to  $NO_X$  in a horizontal axis ] and a vertical axis show the reduction rate (purifying rate) of  $NO_X$ . If equivalent weight of H(mol)  $_2$  is supplied to  $NO_X$ , and  $NO_X$  and  $H_2$  shall be mixed thoroughly, reduction purifying of all the  $NO_X$  will be carried out (theoretical value). However, since complete mixing is not carried out actually, a reduction rate becomes like an experimental value. Although there is a portion to which the purifying rate is good from theory in the experimental value, it is because the steam under exhaust air decomposed on the precious-metals system catalyst and has changed this into  $H_2$ . Therefore, many  $H_2$  reacts to  $NO_X$  from supplied  $H_2$ . [0030]In  $NO_X$  reduction device which performs reduction purifying by  $H_2$  as other examples, it can be considered as the function to install the mixer which carries out mixed mixing of H2 and exhaust air in the entrance side of a reforming catalyst converter. The hydrogen generator and catalyst device which are  $NO_x$ purges of others of this example, Since it has a respectively suitable operating temperature range, a reduction catalyst can be installed in the inside of the muffler to which exhaust air expands and temperature falls at 200 \*\* or less, or its lower stream again in the latter part of the oxidation catalyst which installed the hydrogen generator in the exit of an exhaust manifold in the exhaust system of an internal-combustion

engine.

[0031]In NO<sub>X</sub> reduction device which supplies H<sub>2</sub> of a hydrogen generator and carries out reduction purifying of the NO<sub>X</sub> under engine exhaust gas under O<sub>2</sub> coexistence as other examples, It can have composition which has a means to oxidize HC, such as an oxidation catalyst, a three way component catalyst, and an exhaust air reactor, and CO near an engine exhaust manifold, and uses Pt-zeolitic catalyst for the reforming catalyst converter as a Lean NO<sub>X</sub> catalyst. A sound deadening effect can be given to a reforming catalyst converter, and a reforming catalyst converter and an exhaust air muffler can be considered as unification composition.

[0032]And in NO $_X$  purge which performs NO $_X$  reduction by H $_2$ , it can have composition which installed the soot trapper and the unburnt glow output oxidizing means upstream of the reforming catalyst converter as an object for diesel engines. In this example, a hydrogen fueled engine besides a gasoline engine and a diesel power plant may be sufficient as an internal-combustion engine, and it can be applied effective in these NO $_X$  reduction devices. In the case of this hydrogen fueled engine, a hydrogen generator is not required, and it can be applied by supplying H $_2$  as fuel in bypass via a controller.

### [0033]

[The 1st example] The 1st example that applies the system of this invention to the lean burn engine of the engine displacement 11 is shown in <u>drawing 6</u>. Engine  $E_1$  of the 1st example at the time of the excess air factor lambda= 0.95 at the time of idling - the full load of 1.0 (they are rich side or theoretical air fuel ratio a little than theoretical air fuel ratio) each number of rotations, and rapid acceleration lambda= 0.8-1.0 (rich side), Operating conditions other than this are engine  $E_1$  operated by a thin lambda= 1.2-1.8 side.

Therefore,  $O_2$  under exhaust air changes to about 0 to 10%. Exhaust-system  $E_x$  is composition which installs the oxidation catalyst 9 in the exit of the exhaust manifold 8, oxidizes and purifies incomplete combustion output, such as HC and CO. The reduction catalyst 12 is arranged to the downstream of the muffler 13 as a silencer. In order to equalize mixing with  $H_2$  and exhaust air in the entrance of the reduction catalyst 12, the mixer 10 is formed in it.

[0034]The H<sub>2</sub> generator 11 is a water electrolysis H<sub>2</sub> generator using the reforming catalyst 14, as shown in drawing 7 and drawing 8.

[0035]The hydrogen generator 11 forms the coiled inner core in the branched exhaust pipe, the electromagnetism fuel injection valve which injects methanol is provided in one end of the inner core, and the other end is led to the mixer. It is filled up with porous ceramics for near the entrance of the inner core to evaporate methanol, and the reforming catalyst of the pellet type is got blocked in after that. (When using a monolith-like catalyst, the inner core is changed into linear shape from a coiled form.) The catalyst is using Pd. 15 are a suction-air-quantity sensor which measures the air content to engine  $E_1$  among drawing 6, and 16 is a  $NO_X$  sensor which measures  $NO_X$  concentration under exhaust air.

[0036]Since  $H_2$  of the equivalent is needed by  $NO_X$  and a mol in the case of the 1st example, are based also on  $NO_X$  concentration under exhaust air of engine  $E_1$ , but. In the time of  $H_2$  of 0.3 l/min, and the maximum output maximum horsepower,  $H_2$  of about 1.0 l/min is needed at the time of the vehicle speed of

50 km/h. Although this  $\text{H}_2$  reforms some fuel and it is supplied, The influence which consumption  $\text{H}_2$  under each operating condition has on run fuel consumption is 1 to 2% or less, is a grade which can be disregarded if compared with 15 to 20% of the fuel consumption reduction merit using a lean burn engine, and does not spoil the low-fuel-consumption characteristic of a lean burn engine.

[0037] The methanol which  $H_2$  generating takes is a 0.15 l/min (steam) grade to a 50-km/h run.

[0038]As mentioned above, since the 1st example reforms a little fuel in the  $H_2$  generator 11 and performs  $H_2$ -NO<sub>X</sub> reduction using the low temperature side characteristic of the reduction catalyst 12, It is a practically significant lean burn  $NO_X$  reduction system which can measure reduction of  $NO_X$  regardless of the operation excess air factor lambda of engine  $E_1$ . CO which carries out a byproduction with  $H_2$  is a water gas shift reaction. [0039]

[Formula 5]  $C O + H_2 O \rightarrow H_2 + C O_2$ 

[0040]It comes out, and changes into H<sub>2</sub>, or Pd film separates into H<sub>2</sub> and CO, and there is also the method of supplying ahead of the reduction catalyst 12 as high grade H<sub>2</sub>. However, CO which carries out a byproduction is little, can be committed in the reduction catalyst 12 as a reducing agent as it is, and does not emit CO.

[0041]

[The 2nd example] The 2nd example is a case of the gas engine used for the object for air conditioning, and power generation. Fuel shows the case of natural gas. Unlike the object for cars, the engine for stationing of such a purpose is operated by the number of certain rotations, and fixed load. Therefore, it is easy to keep the temperature of a reforming catalyst converter constant. Since the composition of the 2nd example is almost the same as that of said 1st example as shown in drawing 9, identical parts attach the same agreement and omit explanation.

[0042]Air and natural gas control the fuel supplied to a hydrogen generator by a regulating valve in order to secure required H<sub>2</sub> which is natural gas, is mixed with air and supplied unlike the 1st example. Control is the same as that of said 1st example almost, and does so the almost same operation effect as said 1st example.

[0043]

[The 3rd example]  $NO_X$  reduction device of the engine which combines the device and zeolitic catalyst which reform some fuel and generate  $H_2$  in said each example, and carries out reduction purifying of the  $NO_X$ , It has turned out that a big difference is produced for  $NO_X$  reduction performance according to the conditions of supply of  $H_2$ , and the contents. As shown in <u>drawing 10</u>, exhaust air of the engine containing  $NO_X$  and  $O_2$  is passed for a catalyst, and  $NO_X$  purifying rate at the time of supplying  $H_2$  from the upper stream of a reforming catalyst converter is shown in <u>drawing 11</u>. In <u>drawing 11</u>, a horizontal axis shows the supply rate of  $H_2$  to  $NO_X$ , and 1.0 is a case where  $NO_X$  and  $H_2$  are the equivalents. A vertical axis is the rate that  $NO_X$  is purified by reduction, and 1.0 shows that all  $NO_X$  will be purified.

[0044]When the catalyst 61 of the pellet type shown in <u>drawing 12</u> is contained in the reforming catalyst converter 60 shown in <u>drawing 10</u>, a high purifying rate is shown that <u>drawing 14</u> shows. If the catalyst 62 of the monolith type shown in <u>drawing 13</u> is used, even if it is the same H<sub>2</sub> amount of supply, a purifying rate will fall.

[0045]H<sub>2</sub> and exhaust gas do not mix enough the catalyst 61 of the pellet type shown in <u>drawing 12</u> at the entrance, but even if H<sub>2</sub> has concentration distribution, the crevice between pellets like a maze is enough mixed in the process in which gas is in direct communication and goes, and H<sub>2</sub> and exhaust gas are equalized.

[0046]On the other hand, many section "swage block"-like \*\*\*\* have the catalyst 62 of the monolith type shown in drawing 13.

Since the hole of a piece is in the direction of a gas flow independently, if H<sub>2</sub> has distribution at the entrance, it will be hard to mix the gas in the channel which adjoins each other mutually on the way.

According to the actual experiment, it was difficult to make thickness of an exhaust pipe thick substantially from the restrictions on mount, the gas flow rate was quick, H<sub>2</sub> made the high concentration region near the center section, and H<sub>2</sub> has produced the inconvenience hardly supplied in the monolith periphery.

Therefore, the capacity factor of a monolith type of H<sub>2</sub> is low compared with a pellet type.

[0047]On the other hand, when it sees as an engine exhaust gas system, a pellet's rubbing mutually and it being easy to carry out disintegration by vibration and the direct cross-section area of gas of a pellet type are small, pass resistance is large, and causes exhaust-gas-pressure increase, and there is a fault which gets worse in the engine performance itself. Therefore, although it is desirable to use a monolith type for a catalyst, a device is needed for supply of  $H_2$  in this case.

[0048]Then, the 3rd example comprises the constitutionally simple device which mixes supply of H<sub>2</sub> homogenously so that NO<sub>X</sub> purifying rate which was superior to the pellet type using the catalyst of a monolith type may be acquired. That is, the essential structure of the H<sub>2</sub> jet nozzle 63 as the mixed device 69 is shown in drawing 14 and drawing 15. The inserted H<sub>2</sub> jet nozzle 63 is hollow cylinder shape, and it has turned at it in the shape of an L character to the flow direction of exhaust air.

It has two or more jet holes 64 radiately.

4-6 pieces are suitable for the radiate jet hole 64 -- one row -- or two or more rows are provided. (Three rows of jet holes are allocated in <u>drawing 14</u>).

[0049]D is required for d not less than 20%, and since resistance of a channel will become large if d is enlarged, the insertion tube outer diameter d of the jet nozzle 63 and the inside diameter D of the exhaust pipe 65 carry out section expansion formation of some exhaust pipes 65, as shown in <u>drawing 16</u>. Even if the distance L from the jet nozzle 63 to the reforming catalyst converter 60 needs more than the twice [ at least ] of D and enlarges them 10 or more times, there are few improvement effects. The mixed device can show drawing 17 and <u>drawing 18</u> composition other than \*\*\*\*. that is, the portion which makes H<sub>2</sub> stir comprises the H<sub>2</sub> jet nozzle 66 of a byway, and the cylinder like object with base 68 which established two

or more jet holes 67 in the wall by the major diameter from this -- about two-fold are constituted tubular.  $H_2$  which blew off is first mixed with the exhaust air which flows into the  $H_2$  jet nozzle 66 with the dynamic pressure of exhaust gas pressure, blows off from the container liner of the cylinder like object with base 68 in an outer case, and is further mixed by the exhaust air which flows between inside-and-outside pipes. Thus, since it passes through two steps of mixing processes, about  $H_2$  and exhaust air can mix homogenously thoroughly.

[0050]The size (a diameter or a cross-section area) of an inside-and-outside pipe influences mixing greatly, and if a container liner is small, almost all exhaust air flows through an outer case, and cannot use dynamic pressure enough. In drawing 17 and drawing 18, as for D/d (an outer case/container liner), three to about 1.7 are effective, and the two neighborhoods of the diameter ratio of an inside-and-outside pipe are best. [0051]Mixing becomes good, and even if the 3rd example that consists of the above-mentioned composition is a monolith type, it can acquire the same purifying rate as a pellet type. Since the amount of supply H<sub>2</sub> can be saved 30 to 60% in the same purifying rate, fuel which H<sub>2</sub> generating takes can be lessened and an engine output and the influence on fuel consumption can be reduced.

[0052]For example, if the usual operation area representative point estimates in a 1.6-I. lean burn gasoline engine,  $H_2$  flow taken to purify 2000 rpm of engine speed value and torque 40Nm,  $NO_X$  burst size 0.44 I/min at this time, and this  $NO_X$  by  $H_2$  reduction is 0.66 I/min. The fuel for  $H_2$  generator becomes fuel vapor of 0.33 I/min generating  $H_2$  of 0.66 I/min (in the case of methanol).

[0053]If drawing 17 which is D/d=2, and the device shown in drawing 18 perform mixed promotion, the amount of supply of  $H_2$  can be managed with about 0.44 l/min of  $NO_X$  and equivalent weight, and fuel will fall to the steam of steamy 0.22 l/min of 0.22 l/min. That is, it becomes saving of 0.11 l/min. [0054]

[The 4th example] In said example, hydrogen is generated with a hydrogen generator using a zeolitic catalyst, and if  $H_2$  is supplied to the entrance of a zeolitic catalyst and  $NO_X$  reduction by  $H_2$  is performed, even if high-concentration  $O_2$  exists during exhaust air, big  $NO_X$  purifying rate is acquired.

[0055]However, compared with the conventional NO<sub>X</sub> catalyst, for example, a three way component catalyst, and Cu-zeolitic catalyst, it is a low-temperature reaction, Compared with the conventional catalyst using the space velocity (ratio of passing gas flow I/hr to the catalyst body product I) 50,000-100,000, SV (for example, 10,000-60,000) small from the relation of reaction velocity must be used. When mounting this system, the reforming catalyst converter of this system consists of inlet gas temperature, the lower stream, for example, near an exhaust air muffler, an exhaust system. However, it is a place in which the large (the size of a converter is large) reforming catalyst converter of car structure top space velocity is installed in a car, and is hard to apply to all the cars.

[0056]Since the 4th example makes installation of a reforming catalyst converter easy, even if it makes a catalyst build in the muffler structure and the muffler for making a Lean  $NO_X$  catalyst build in a muffler, and measuring miniaturization, it enables  $NO_X$  purification from temperature conditions.

[0057]That is, since the composition of the 4th example can be managed with one of the two, without

arranging NO<sub>X</sub> converter and an exhaust air muffler in series if the Lean NO<sub>X</sub> catalyst 82 is made to build in the exhaust air muffler 80 as shown in <u>drawing 20</u> and <u>drawing 21</u>, it becomes very [ in disposition space ] advantageous. The reforming catalyst converter 83 which gave the sound deadening effect which built the monolithic catalyst 82 (Pt-zeolite system) in the exhaust air muffler 80 is shown in <u>drawing 20</u> and <u>drawing 21</u>.

[0058]While the exhaust air by which mixing mixing was carried out in H<sub>2</sub> flows from an arrow direction, it collides with the mixing plate 84, it passes through the circulating hole 85 of size plurality of this mixing plate 84 and exhaust air and H<sub>2</sub> are enough mixed from the upper stream of the reforming catalyst converter 83, it flows into the monolithic catalyst 82. Since the circulating hole 85 is not established in the central part which becomes the exhaust flow rate maximum on the mixing plate 84, H<sub>2</sub> does not concentrate on the monolith central part, the circulating hole 85 of the mixing plate 84 -- each size -- it differs in a diameter, and since multiple arrays are carried out, passing flow velocities differ, stirring of gas takes place, and a sound deadening effect is done so by interference.

[0059]By the way, as for an exhaust air muffler, it is common to be arranged in engine-exhaust-systems Osamu's tail end, and since it is cooled on the way, the inlet gas temperature of an exhaust air muffler becomes low. It is 150-200 \*\* also in the time of the maximum-engine-speed maximum horsepower of an engine with the highest inlet temperature, and is about 100-150 \*\* in an operating condition with high normal use frequency.

[0060]Since sufficient reaction is not expectable unless it is not less than 300-400 \*\*, a catalyst cannot be made to build in in a muffler with the conventional three way component catalyst or the Lean  $NO_X$  catalyst of a Cu-zeolite system. In said example, when performing reduction by  $H_2$ , it was shown that it can purify at low temperature, but temperature is about 150-300 \*\*, and if compared with the inlet temperature of an exhaust air muffler, it is in a little high temperature requirement.

[0061]This invention persons examined [ various ] experimentally what should be selected as a catalyst component about the activity of  $NO_X$  reduction catalyst which supplies  $H_2$  under  $O_2$  coexistence. As a result, Pd and Rh did not have activity, activity of Cu was bad, and Pt found out that high activity was shown. However, Pt needs to be high distribution and carriers which have high specific surface area (more than at least  $100-m^2/g$ ) for that purpose, such as alumina, silica, and zeolite, are required for it.

[0062]this invention persons considered pretreatment which should be performed before the Lean NO<sub>X</sub>

catalyst of  $NO_X$  reduction, and  $H_2$  mixing by boiling many things. The result is shown in drawing 19. When

 $H_2$  is mixed to engine exhaust air and it leads to the Lean  $NO_X$  catalyst (Pt system) of  $NO_X$  reduction, as shown in the curve B, the peak of activity is near 250 \*\* among drawing 19.

[0063]An afterburner, a reactor, a three way component catalyst, an oxidation catalyst, etc. are established near an engine manifold, When H<sub>2</sub> was supplied and it led to the reforming catalyst converter of NO<sub>X</sub> reduction after oxidizing and carrying out reduction removal of CO and the HC beforehand, as shown in the curve A in drawing 19, active temperature shifted to the low temperature side, and it newly found out that high activity was shown at 100-150 \*\*.

[0064]In accordance with the inlet temperature of an exhaust air muffler, this temperature was closed, if

possible [ for the first time ] by building in the reduction catalyst 80 of a Pt-zeolite system in the exhaust air muffler 80. After removing HC and CO, the direction which performed  $NO_X$  purification by a Lean  $NO_X$  catalyst can also improve a purifying rate, and does so the practically outstanding operation effect which does not form soot on a catalyst from the imperfect reaction of HC- $O_2$ .

[0065]The sound deadening effect is made more into fitness by installing interference tube Ex1 after the monolithic catalyst 82. Drawing 22 does so the same operation effect as drawing 20 and drawing 21, and differs in the gestalt of a mixer part with said mixing plate, and the points used as the mixing pipe 86 which is a hollow cylindrical member differ. Since the reforming catalyst converter 83 and the exhaust air muffler 80 can consider the 4th example that consists of the above-mentioned composition as unification composition, it does so the practical effect that it becomes compact and mount nature becomes good, and it does so the outstanding effect which can maintain high NO<sub>x</sub> purifying rate in the whole drive range.

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### **TECHNICAL FIELD**

[Industrial Application]In what is called the lean burn engine and the diesel power plant, other hydrogen fueled engines, etc. which this invention requires for the nitrogen-oxides reduction device of an internal-combustion engine, and use a lean mixture and aim at the improvement in fuel consumption especially, without it spoils the goodness of the fuel consumption of the engine concerned -- the concentration of the oxygen gas (O<sub>2</sub> is called below) under exhaust air -- it is related with the Lean NO<sub>X</sub> catalyst exhaust gas cleaning system which can carry out reduction purifying of the nitrogen oxides (NO<sub>X</sub> is called below) effectively regardless of how.

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### **PRIOR ART**

[Description of the Prior Art]In a piston engine, as an internal-combustion engine and the Lord, to the reducing method of the nitrogen oxides (NO $_{\rm X}$  is called below) of exhaust air. The NO $_{\rm X}$  decreasing method by the use \*\* Lean  $NO_X$  catalyst of the  $NO_X$  decreasing method \*\* super-rarefaction air-fuel ratio by the former and \*\* three way component catalyst (for example, JP,1-139145,A) Three \*\* are considered. However, the weight ratio of the fuel in which the method of \*\* is supplied to an engine, and air must be about 14.5, i.e., theoretical air fuel ratio. If fuel uses a thin air-fuel ratio from theoretical air fuel ratio,  $\mathsf{NO}_\mathsf{X}$  does not decrease. However, it is known that considering the economical efficiency of fuel consumption specific fuel consumption has few directions which operated the engine by the thin side from theoretical air fuel ratio as shown in drawing 2, and it is efficient. [0003]Next, \*\* tends to reconcile  $NO_X$  reduction and fuel consumption reduction with what is called a lean burn engine. However, if it tries to use the air-fuel ratio which can reduce  $NO_{\chi}$  enough, it approaches the misfire limit of combustion, and engine fuel consumption not only worsens, but it will be ruined and drivability will worsen. In order to prevent this, disorder and the increase in the rate of flow are measured with the air flow in a cylinder, the rate of combustion is made quick and there are some which are going to improve a misfire limit so that it may become a thin region more. However, since the flame kernel formation at the time of ignition and the flame propagation in early stages of combustion will be barred on the contrary if air disorder and the increase in the rate of flow are performed too much, there is a limit in expansion of the misfire limit by this method. Although there is also the method of making it into the rich mixture which adjusted the air-fuel ratio distribution in a cylinder and to which only the neighborhood of an ignition plug was suitable for ignition, since the decreasing rate will decrease as the dashed line also showed generating  $NO_\chi$ if a misfire limit spreads to a thin side more as shown in drawing 3, a big effect is not expectable. [0004]\*\* In order to compensate the fault of the above-mentioned \*\*, it is going to operate using near [ slightly near theoretical air fuel ratio ] a specific-fuel-consumption minimum score from a misfire limit, and  $NO_x$  in which reduction is a little insufficient tends to purify with a zeolite system Lean  $NO_x$  catalyst. This method may become a fuel-efficient system. However, there is a problem which should be solved practically that  $NO_X$  purifying rate and endurance of catalyst this Lean  $NO_X$  catalyst will return  $NO_X$  under a lot of  $O_2$ 

existence during exhaust air, severe [ a catalyst ] temperature conditions etc. and sufficient under the

present circumstances can be easily incompatible. The method of reducing NO<sub>X</sub> enough all has many practical problems, using the air-fuel ratio which can make engine specific fuel consumption small as much as possible as mentioned above.

[0005]By the way, although it is fundamentally the same that excess  $O_2$  is included during exhaust air also by the lean burn engine or a diesel power plant,  $O_2$  concentration becomes large, so that exhaust air of this engine uses a lean mixture including  $O_2$  during exhaust air. The catalyst which performs  $NO_X$  reduction purifying under exhaust air containing such  $O_2$  is called Lean  $NO_X$  catalyst, and the catalyst of a preciousmetals system, for example, a zeolite system, is used in many cases. In this Lean  $NO_X$  catalyst, the relation between  $NO_X$  purifying rate and temperature shows drawing 4. And a not less than 350 \*\* pyrosphere is mainly a reaction of  $HC-NO_X$ . A low temperature region 250-350 \*\* or less serves as a reduction reaction by  $H_2$  of  $NO_X$ , and purification of  $NO_X$  is possible for it.

[0006]However, since an exhaust-gas temperature amounts also to a maximum of 800-900 \*\* since a Lean NO<sub>X</sub> catalyst is installed near an engine exhaust manifold, and an air-fuel ratio uses a thin side from theoretical air fuel ratio in exhaust air of a lean burn engine, H<sub>2</sub> hardly exists during exhaust air. Therefore, the characteristic by the side of low temperature was a field which cannot be used conventionally.

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### EFFECT OF THE INVENTION

[Function and Effect]NO<sub>X</sub> reduction device of the internal-combustion engine of this invention which consists of the above-mentioned composition does the following operations so.

[0010]Namely,  $NO_X$  reduction device of the internal-combustion engine of this invention which this invention person etc. invented, The basis of the existence of  $NO_X$  and  $O_2$  during exhaust air according to combustion of supply fuel in the combustion chamber of an internal-combustion engine by having composition as shown in drawing 1, Carry out the catalytic reaction of  $H_2$  and the  $NO_X$ , and to the entrance side of nitrogen gas and the catalyst device formed in the exhaust system decomposed into water Methanol or LPG,  $H_2$  from the hydrogen generator which leads some hydrocarbon fuel, such as natural gas, to a reforming catalyst converter, and generates  $H_2$  is supplied, The operation effect which carries out direct reduction purification of the  $NO_X$  under said exhaust air exactly efficiently by this  $H_2$  under the exhaust air low temperature atmosphere in near the silencer of an exhaust system, and reduces this  $NO_X$  is done so. For this reason,  $NO_X$  reduction device of the internal-combustion engine of this invention, Since an engine operating air-fuel ratio can reduce  $NO_X$  according to a catalyst regardless of the concentration of existence of  $O_2$  a thin side and under exhaust air, or  $O_2$  from a rich side, theoretical air fuel ratio, and theoretical air fuel ratio, from theoretical air fuel ratio On engine (car) performance, The profitableness which can choose an optimum value without taking into consideration fuel consumption top  $NO_X$  reduction conditions can be given.

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### **TECHNICAL PROBLEM**

[Problem(s) to be Solved by the Invention] The purpose of this invention is what solves the above-mentioned conventional various problems, Without spoiling the goodness of the fuel consumption of a lean burn engine or a diesel power plant under coexistence of  $NO_X$  and  $O_2$  during exhaust air of a lean burn engine or the diesel power plant always operated by the  $Oover_2$  (air) side, the concentration of  $O_2$  under exhaust air -- it is going to provide  $NO_X$  reduction device of the exhaust gas cleaning system, i.e., the internal-combustion engine which can control the burst size of  $NO_X$ , which carries out reduction purifying of the  $NO_X$  effectively regardless of how.

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### **MEANS**

[Means for Solving the Problem] $\mathrm{NO}_{\mathrm{X}}$  reduction device of an internal-combustion engine of this invention, A basis of existence of  $\mathrm{NO}_{\mathrm{X}}$  and  $\mathrm{O}_{\mathrm{2}}$  during exhaust air by combustion of fuel supplied from a fuel supply system in a combustion chamber of an internal-combustion engine, Form a catalyst device for carrying out catalytic reaction of  $\mathrm{H}_{\mathrm{2}}$  and the  $\mathrm{NO}_{\mathrm{X}}$  within an exhaust system, and purifying  $\mathrm{NO}_{\mathrm{X}}$ , and. Provide a hydrogen generator which generates hydrogen by a reforming catalyst converter for some hydrocarbon fuel, such as methanol or LPG, and natural gas, in an entrance side of this catalyst device, and  $\mathrm{H}_{\mathrm{2}}$  is constituted so that supply is possible, It is the composition of carrying out direct reduction purification of the  $\mathrm{NO}_{\mathrm{X}}$  under said exhaust air by  $\mathrm{H}_{\mathrm{2}}$  from this hydrogen generator under an exhaust air low temperature atmosphere in near the silencer of an exhaust system, and having reduced this  $\mathrm{NO}_{\mathrm{X}}$ .

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### **EXAMPLE**

[Example]A reforming catalyst converter is classified according to the fuel which uses the hydrogen generator in an example for an engine as follows.

[0012]That is, if it is in the engine which uses methanol as fuel, the gas which carried out heating evaporation of the methanol by exhaust air is led to this catalyst using transition metal catalysts, such as 1Pd, Pt, and Cu/Cr/nickel, and H<sub>2</sub> is generated. About 300 \*\* is best and catalyst inlet gas temperature is a reaction at this time. [0013]

[Formula 1] 
$$C H_3 O H \rightarrow C O + 2 H_2$$

### [0014]It becomes.

[0015]2) Make methanol vapour mix air, according to Cu-nickel-Cr/alumina catalyst, carry out partial oxidation of some methanol, and generate H<sub>2</sub>. 400 \*\* - 500 \*\* are suitable for temperature, it controls the air flow rate made to mix in methanol, and maintains temperature. The reaction in this case, [0016] [Formula 2]

$$CH_3OH + Air \rightarrow H_2 + CO + H_2O$$

# [0017]It becomes.

[0018]3) Cu-Mn or Cu-Zn is used for a catalyst, and add a steam to methanol, or add air and methanol water, and perform steam reforming. About 250 \*\* is suitable and temperature is a reaction. [0019] [Formula 3]

# [0020]It becomes.

[0021]If it is in the engine using hydrocarbon fuel, such as LPG and natural gas, nickel, CO, and Rh are used as a catalyst and it reforms at the temperature of 300-800 \*\*. In the case of this hydrocarbon fuel, the water from a steam, air, or a water tank is added, and refining is carried out to it. (Temperature changes with catalysts.) There is much methane at low temperature and there is much CO at an elevated temperature. As a reaction, [0022]

[Formula 4]

$$HC + H_2 O \rightarrow H_2 + CH_4 + CO_2 300~500$$
  $^{\circ}$   $^{\circ}$ 

### [0023]It becomes.

[0026]And since NO<sub>X</sub> reduction device of the internal-combustion engine of this example makes mixing of H<sub>2</sub> and exhaust air uniform in the entrance side of said catalyst device, it can possess a mixer or can also consider it as the composition which uses the silencer of an exhaust system effectively.

[0027]If it explains in full detail,  $NO_X$  reduction device of the internal-combustion engine of this example was invented in order to solve said conventional problem, and shows <u>drawing 1</u> the basic constitution figure. That is, the 1st point of this example is that this  $H_2$  reduction uses it in the whole drive range of the engine E by the exhaust air low temperature side. The 2nd point is incorporating the  $H_2$  generator 1 into a constitution system in order to enable use by the side of low temperature. The 3rd point is controlling the  $H_2$  generator 1 by the operational status of the engine E, or the amount of  $NO_X$  under exhaust air, and enabling it to always supply an equivalent grade or superfluous  $H_2$  by  $NO_X$  and a mol during exhaust air.

[0028]Since  $H_2$  will react to  $O_2$  and the selectivity of  $H_2$ -NO $_X$  will be lost if exposed to an elevated temperature, the reduction catalyst 2 is arranged near the silencer 3 so that it may not be exposed to not less than 350 \*\*. And this example branches from fuel piping, carries out introductory reforming of the fuel via a flow control valve at the reforming catalyst converter as an  $H_2$  generator, and generates  $H_2$ .  $H_2$  is supplied near the entrance of the reduction catalyst 2. In order to make  $H_2$  to supply into an equivalent grade by  $NO_X$  and the mol under exhaust air, an air content is measured by the suction-air-quantity sensor 5

of the engine E, boil  $NO_X$  concentration under exhaust air  $NO_X$  sensor 6, after asking for \*\*\*\* and calculating  $NO_X$  flow from the output of both the sensors 5 and 6 by the controller 7, It is the composition which controls the air valve for refining by the fuel flow introduced into a reforming catalyst converter in order to generate  $H_2$  corresponding to  $NO_X$  flow, and the thing which performs reforming catalyst converter temperature by an exhaust air flow dividing valve, and partial oxidation.

[0029]In drawing 5, the delivery late of  $H_2$  [ as opposed to  $NO_X$  in a horizontal axis ] and a vertical axis show the reduction rate (purifying rate) of  $NO_X$ . If equivalent weight of  $H(mol)_2$  is supplied to  $NO_X$ , and  $NO_X$  and  $H_2$  shall be mixed thoroughly, reduction purifying of all the  $NO_X$  will be carried out (theoretical value).

However, since complete mixing is not carried out actually, a reduction rate becomes like an experimental value. Although there is a portion to which the purifying rate is good from theory in the experimental value, it is because the steam under exhaust air decomposed on the precious-metals system catalyst and has changed this into  $\rm H_2$ . Therefore, many  $\rm H_2$  reacts to  $\rm NO_X$  from supplied  $\rm H_2$ .

[0030]In  $NO_X$  reduction device which performs reduction purifying by  $H_2$  as other examples, it can be considered as the function to install the mixer which carries out mixed mixing of  $H_2$  and exhaust air in the entrance side of a reforming catalyst converter. The hydrogen generator and catalyst device which are  $NO_X$  purges of others of this example, Since it has a respectively suitable operating temperature range, a reduction catalyst can be installed in the inside of the muffler to which exhaust air expands and temperature falls at 200 \*\* or less, or its lower stream again in the latter part of the oxidation catalyst which installed the hydrogen generator in the exit of an exhaust manifold in the exhaust system of an internal-combustion engine.

[0031]In  $NO_X$  reduction device which supplies  $H_2$  of a hydrogen generator and carries out reduction purifying of the  $NO_X$  under engine exhaust gas under  $O_2$  coexistence as other examples, It can have composition which has a means to oxidize HC, such as an oxidation catalyst, a three way component catalyst, and an exhaust air reactor, and CO near an engine exhaust manifold, and uses Pt-zeolitic catalyst for the reforming catalyst converter as a Lean  $NO_X$  catalyst. A sound deadening effect can be given to a reforming catalyst converter, and a reforming catalyst converter and an exhaust air muffler can be considered as unification composition.

[0032]And in  $NO_X$  purge which performs  $NO_X$  reduction by  $H_2$ , it can have composition which installed the soot trapper and the unburnt glow output oxidizing means upstream of the reforming catalyst converter as an object for diesel engines. In this example, a hydrogen fueled engine besides a gasoline engine and a diesel power plant may be sufficient as an internal-combustion engine, and it can be applied effective in these  $NO_X$  reduction devices. In the case of this hydrogen fueled engine, a hydrogen generator is not required, and it can be applied by supplying  $H_2$  as fuel in bypass via a controller.

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### **DESCRIPTION OF DRAWINGS**

[Brief Description of the Drawings]

[Drawing 1]The lineblock diagram showing the basic constitution of the example of this invention

[Drawing 2]The diagram showing an air-fuel ratio and the relation of a fuel economy

[Drawing 3]The diagram showing the fuel consumption of a lean burn engine, and the relation of  $NO_X$ 

[Drawing 4]The diagram showing the characteristic of a Lean NO<sub>X</sub> catalyst

[Drawing 5] The diagram showing the relation between  $H_2$  supply rate and  $NO_X$  purifying rate

[Drawing 6]The lineblock diagram showing the outline of the 1st example device of this invention

[Drawing 7]The sectional view of  ${\rm H_2}$  generator in the 1st example device

[Drawing 8]The lineblock diagram expanding and showing the important section of H<sub>2</sub> generator of others in

the 1st example device

[Drawing 9]The lineblock diagram showing the outline of the 2nd example device of this invention

[Drawing 10]The lineblock diagram showing the outline of the 3rd example device of this invention

[Drawing 11] The diagram showing the relation of  $NO_X$  purifying rate about the 3rd example device

[Drawing 12]The schematic diagram showing pellet type catalyst composition about the 3rd example device

[Drawing 13]The schematic diagram showing the catalyst composition of a monolith type about the 3rd example device

[Drawing 14]Drawing of longitudinal section showing the outline of the 3rd example device of this invention

[Drawing 15]The cross-sectional view showing the outline of the 3rd example device of this invention

[Drawing 16]The schematic diagram showing the outline of the 3rd example device of this invention

[Drawing 17]Drawing of longitudinal section showing the example of others of the 3rd example device of this invention

[Drawing 18] The cross-sectional view showing the example of others of the 3rd example device of this invention

[Drawing 19] The diagram showing  $NO_X$  purifying rate situation about the 4th example of this invention

[Drawing 20]Drawing of longitudinal section showing the outline of the 4th example device of this invention

[Drawing 21]The cross-sectional view showing the outline of the 4th example device of this invention

[Drawing 22]Drawing of longitudinal section showing the composition of others of the 4th example device of

this invention

[Description of Notations] E, E<sub>1</sub> engine

1 and 11 H<sub>2</sub> generator 3, 13, and 80 Silencer

12 and 60 Reduction catalyst

9 Oxidation catalyst

5 Suction-air-quantity sensor

 $6~\mathrm{NO_X}$  sensor

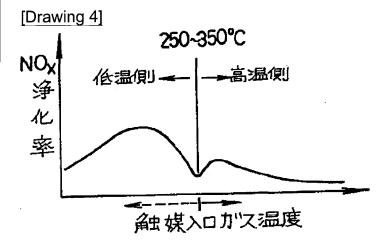
7 Control power supply

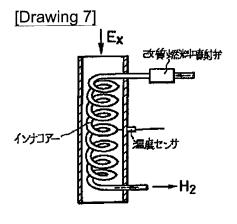
10 Mixer

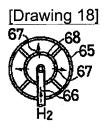
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- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

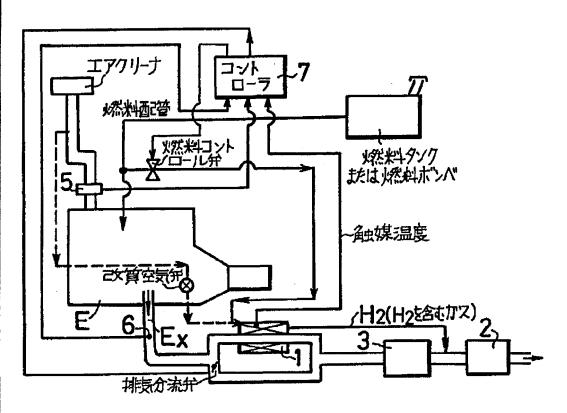
## **DRAWINGS**

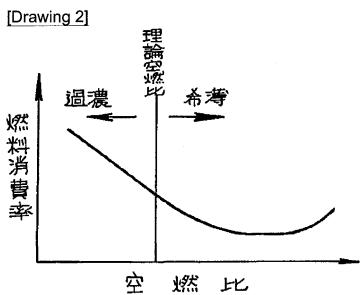


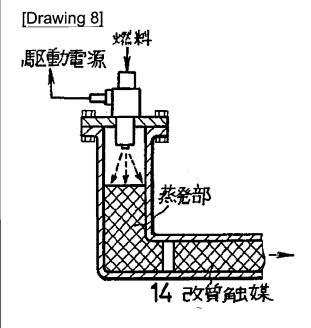


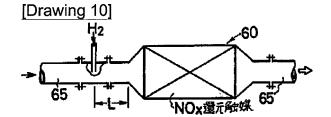


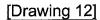
[Drawing 1]











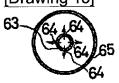


[Drawing 13]

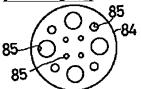




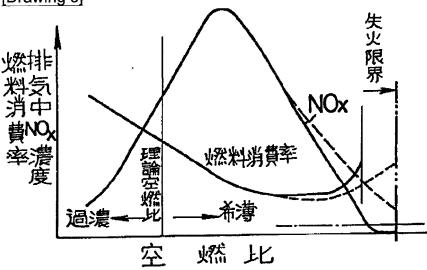
# [Drawing 15]

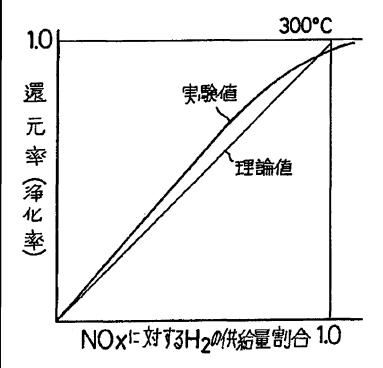


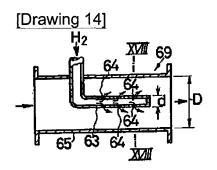
# [Drawing 21]

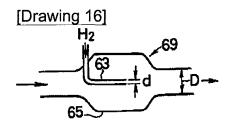


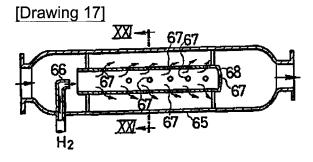












[Drawing 20]

